Journal of Chromatography, 270 (1983) 181–189
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,081

GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XX*. UNSATURATED ALCOHOLS AND THE CORRESPONDING ESTERS OF PROPANOIC AND BUTANOIC ACIDS AND THEIR MONOCHLORINATED DERIVATIVES

ILPO O. O. KORHONEN
Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)
(Received June 25th, 1983)

SUMMARY

The gas chromatography of 2-propen-1-ol, 2-propyn-1-ol, 3-buten-1-ol, 4-penten-2-ol, 4-penten-1-ol and *trans*-, and *cis*-3-hexen-1-ol and their propanoyl, 2- and 3-chloropropanoyl, butanoyl and 2-, 3- and 4-chlorobutanoyl derivatives has been studied on SE-30 and OV-351 capillary columns with programmed temperature rise. The alcohols and their esters are eluted in the same order on both non-polar and polar columns, whereas quite different elution orders of the individual components in mixtures of the alcohols and their C_3- and C_4-derivatives are observed on the columns used. In this respect 2-propyn-1-ol and its esters are the most diverging compounds, the alcohol having a retention time on OV-351 of over three times that on SE-30. Retention data for 56 compounds are given and the results are compared with those reported previously for the saturated alcohols and their derivatives.

INTRODUCTION

Earlier parts of this series dealt with the gas chromatographic (GC) separations of mixtures of aliphatic straight- and branched-chain alcohols and the corresponding alkyl esters of propanoic, monochloropropanoic, butanoic and monochlorobutanoic acids[1–3].

Although the GC separation of aliphatic saturated straight- and branched-chain alcohols has been widely investigated[1–3], a systematic GC study of the unsaturated alcohols has obviously not been reported. The retention behaviour of alkanoic and alkenoic esters has been extensively studied, *e.g.*, by Ashes and Haken[4,5], who reported that the relative incremental effects of the chain parameters have a greater effect on retention when in the alkyl rather than the acyl chain. The GC separation of the esters of unsaturated alcohols has been shown little interest in the literature. However, the structure–retention increments of *trans*- and *cis*-2-hexenyl and 3-hex-

* For Part XIX, see ref. 3.

0021-9673/83/$03.00

enyl esters of aliphatic C_1–C_6 *n*-acids, as well as of the acetyl derivatives of some C_5–C_{10} unsaturated alcohols have been reported by Ashes and Haken[5].

The present work reports the retention behaviour of some unsaturated alcohols and their propanoyl, 2- and 3-chloropropanoyl, butanoyl and 2-, 3- and 4-chlorobutanoyl derivatives, extending the previous work with saturated alcohols and their derivatives[1–3]. The retention data of the compounds on non-polar SE-30 and polar OV-351 quartz capillary columns are given and the separation of the individual components in the complex mixtures of the alcohols and their C_3- and C_4-esters is discussed. The results are compared with those of the saturated homologues reported earlier[1–3].

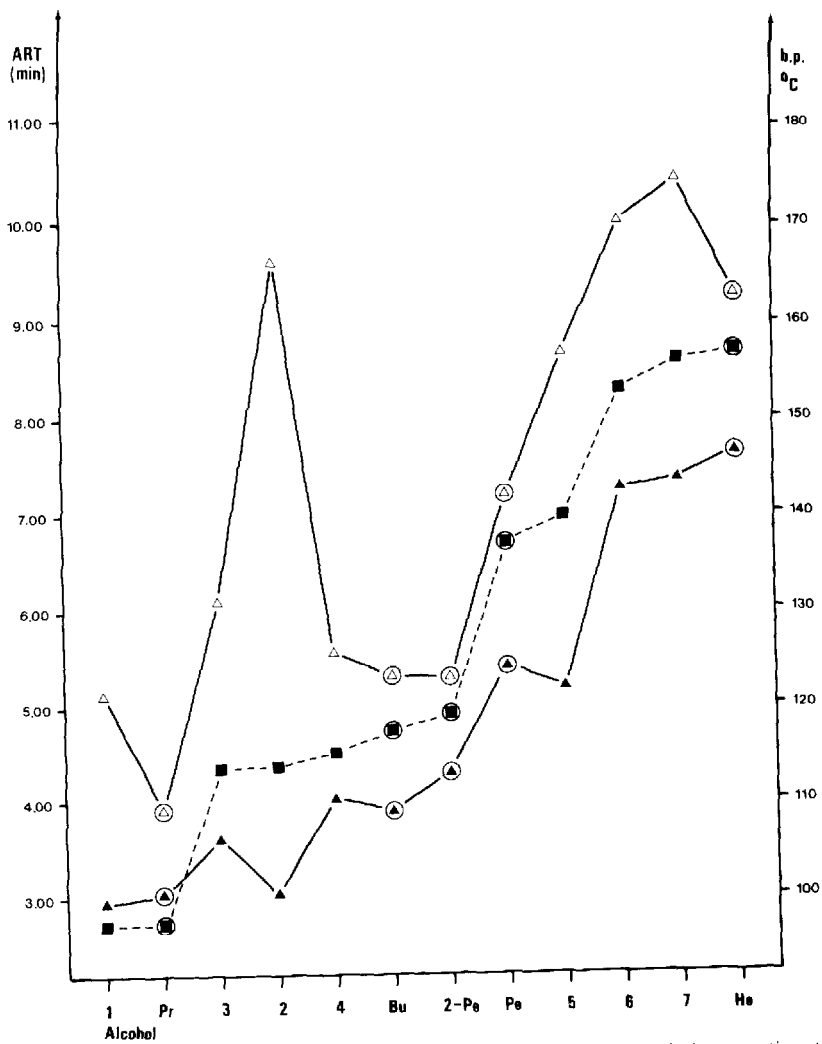

Fig. 1. Correlation between the boiling points (b.p.) (■ - ■) and the retention times (ART) of the unsaturated alcohols (1–7) and the corresponding saturated homologues[2,3], analysed on SE-30 (▲—▲) and OV-351 (△—△). Pr = 1-Propanol, Bu = 1-butanol, 2-Pe = 2-pentanol, Pe = 1-pentanol, He = 1-hexanol; the alcohols (1–7) are identified in Table I.

EXPERIMENTAL

Materials and methods

2-Propyn-1-ol (2), 3-buten-1-ol (3), 4-penten-2-ol (4), 4-penten-1-ol (5) and *n*-tetradecane (57) were commercial products (Fluka, Buchs, Switzerland), whereas 2-propen-1-ol (1) and the mixture of *trans*- and *cis*-3-hexen-1-ols (6 and 7) were the products of Merck-Schuchardt (F.R.G.). Alkenyl and alkynyl propanoates (8–14), 2-chloropropanoates (15–21), 3-chloropropanoates (22–28), butanoates (29–35), 2-chlorobutanoates (36–42), 3-chlorobutanoates (43–49) and 4-chlorobutanoates (50–56) were prepared from the unsaturated alcohols (1–7) and acid chlorides as described earlier[1,2].

The GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the operating conditions reported previously[2]. The column (SE-30 and OV-351) temperature was programmed from 50°C at 6°C/min, until elution of peaks had ceased. All retention times were measured from sample injection, the chromatographic data being analysed with a Hewlett-Packard Model 3390A reporting integrator, using standard programs.

RESULTS AND DISCUSSION

Fig. 1 shows the correlation between the boiling points and the retention times

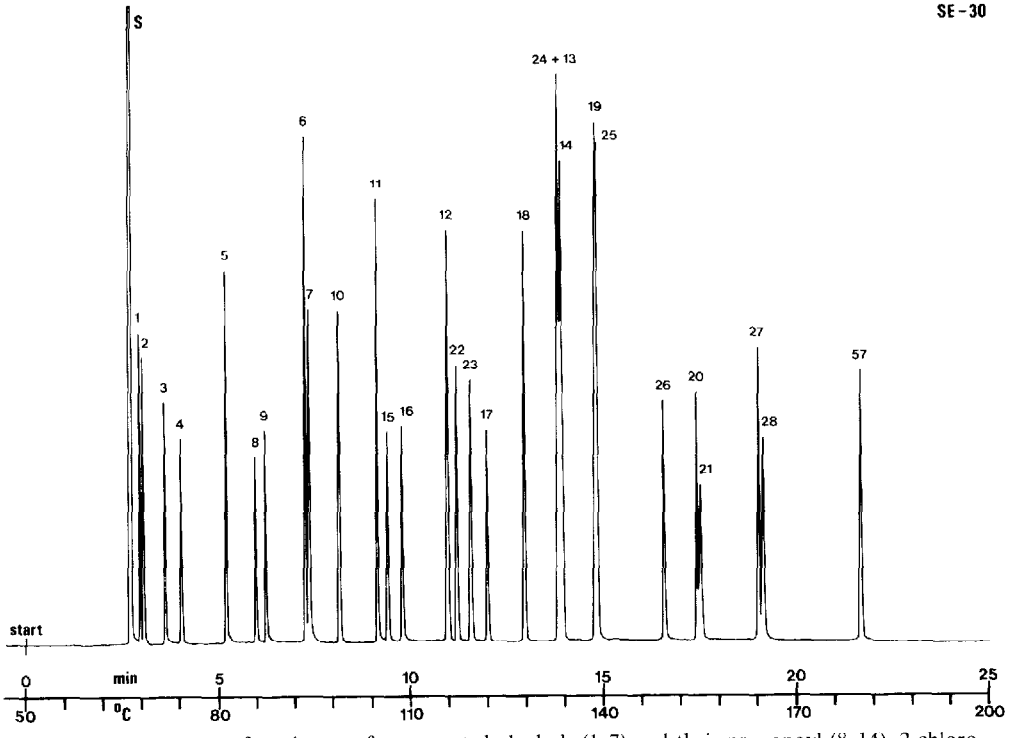

Fig. 2. Chromatogram of a mixture of unsaturated alcohols (1–7) and their propanoyl (8–14), 2-chloropropanoyl (15–21) and 3-chloropropanoyl derivatives (22–28), analysed on SE-30. S = Solvent, *n*-tetradecane (57); compounds are identified in Table I.

of the unsaturated alcohols (1–7) studied in the present work and of the corresponding saturated alcohols reported earlier[2,3]. As shown, a relatively short retention time is observed for 2-propyn-1-ol (2) on SE-30, the compound being eluted at the same time as 1-propanol and clearly earlier than 3-buten-1-ol (3) in spite of the almost equal boiling points of the unsaturated alcohols (113.6 and 113.5°C, respectively). 2-Propyn-1-ol (2), however, shows on OV-351 a retention time over three times that on SE-30, the alcohol being eluted between 1-hexanol[2] and *trans*-3-hexen-1-ol (6) in spite of the high boiling points of these alcohols (157 and 153°C, respectively). By contrast, the only secondary unsaturated alcohol studied, *i.e.*, 4-penten-2-ol (4), is eluted earlier than the closely related 3-buten-1-ol (3) on a polar column. As shown, the boiling point of the saturated alcohols is, except for 1-pentanol, higher than that of the corresponding unsaturated alcohols, the latter being eluted on a non-polar column first [2-propyn-1-ol (2) excluded]. On OV-351, however, all the alcohol pairs studied are eluted in the reverse order to that on SE-30, 1-pentanol and 4-penten-1-ol (5) appearing in the order according to their boiling points (Fig. 1). As expected, a greater disparity between the retention times of *trans*- and *cis*-3-hexen-1-ols (6 and 7) are observed on OV-351 than on SE-30, the alcohols being eluted in the same order on both columns.

Figs. 2 and 3 show the GC separations of a mixture of unsaturated alcohols (1–7) and their propanoyl (8–14) and monochloropropanoyl derivatives (15–28), an-

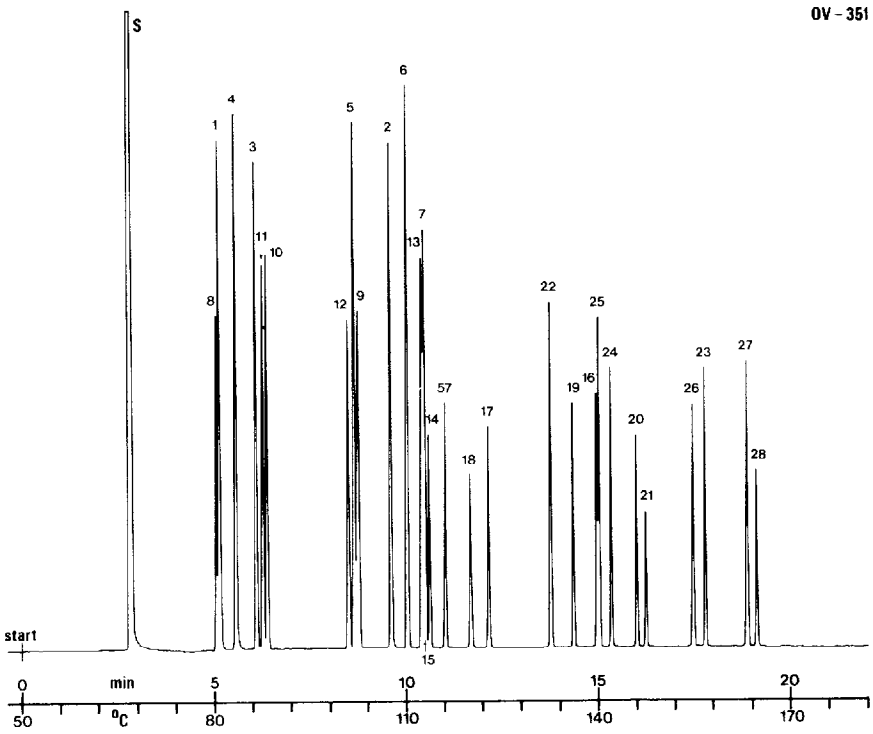

Fig. 3. Chromatogram of a mixture of unsaturated alcohols (1–7) and their propanoyl (8–14), 2-chloropropanoyl (15–21) and 3-chloropropanoyl derivatives (22–28), analysed on OV-351. S = Solvent, *n*-tetradecane (57); compounds are identified in Table I.

alysed on SE-30 and OV-351, respectively. The corresponding chromatograms of a mixture of alcohols (1–7) and their butanoyl (29–35) and monochlorobutanoyl derivatives (36–56) are illustrated in Figs. 4 and 5. The retention data of all 56 compounds studied are presented in Table I, the retention times being tabulated relative to *n*-tetradecane, to the corresponding alcohol and to the corresponding unchlorinated ester. The retention times are also expressed as the ratios of the retention times of the compounds on OV-351 divided by those on SE-30.

Figs. 2–5 show that the esters of the unsaturated alcohols are eluted in the same order as the unsaturated alcohols on both the polar and non-polar capillary columns used. The alcohols are always eluted on SE-30 earlier than their propanoyl derivatives (Fig. 2), whereas on OV-351 2-propenyl propanoate (8), 4-pentenyl propanoate (12) and 2-propynyl propanoate (9) are eluted earlier than the corresponding alcohols (1, 5 and 2). Owing to the relatively higher boiling points of the C_4-esters, the corresponding reverse elution orders on OV-351 do not occur (Fig. 5).

Fig. 2 shows that the peaks of 3-butenyl 3-chloropropanoate (24) and *trans*-3-hexenyl propanoate (13) overlap on SE-30, the *trans*- and *cis*-3-hexen-1-ols (6 and 7) and their derivatives (13 and 14, 20 and 21, and 27 and 28) partially overlapping, as do those for 4-pentenyl 2-chloropropanoate (19) and 1-methyl-3-butenyl 3-chloropropanoate (25). A highly-polar OV-351 column proved to be more efficient for the separation of the mixture, as shown in Fig. 3. Certainly, 2-propenyl 2-chloro-

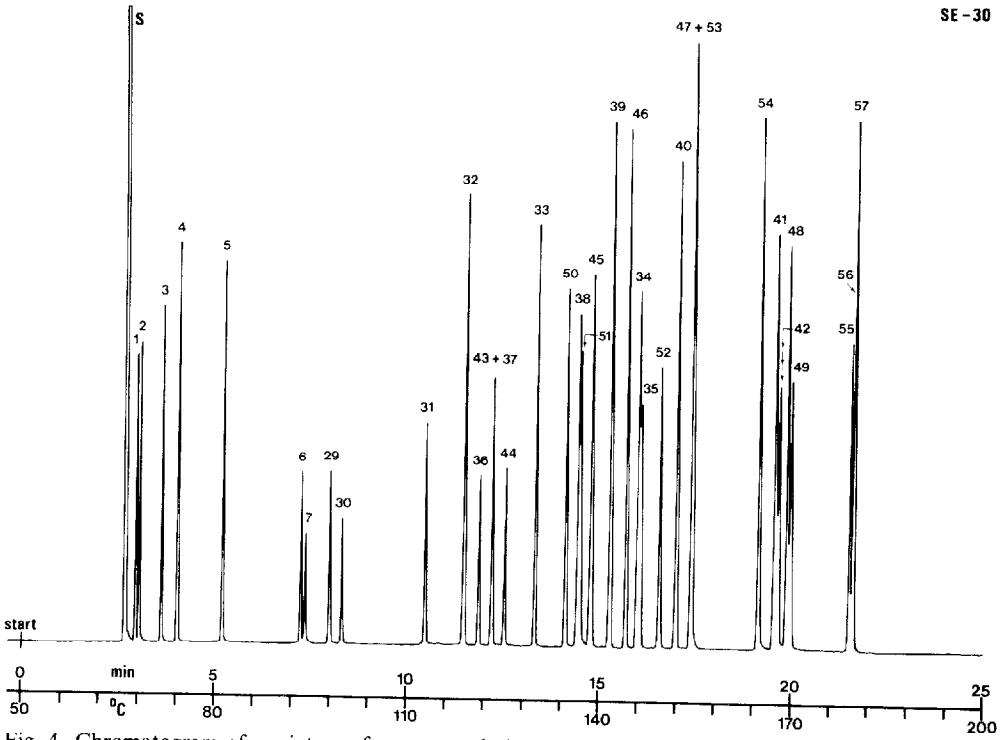

Fig. 4. Chromatogram of a mixture of unsaturated alcohols (1–7) and their butanoyl (29–35), 2-chlorobutanoyl (36–42), 3-chlorobutanoyl (43–49) and 4-chlorobutanoyl derivatives (50–56), analysed on SE-30. S = Solvent, *n*-tetradecane (57); compounds are identified in Table I.

TABLE I

RETENTION DATA OF UNSATURATED ALCOHOLS AND THEIR PROPANOYL, MONOCHLOROPROPANOYL, BUTANOYL AND MONOCHLOROBUTANOYL DERIVATIVES, ANALYSED ON SE-30 AND OV-351 CAPILLARY COLUMNS

Conditions as shown in Figs. 2–5.

Peak No.	*Compound*	*Column*								
		SE-30				*OV-351*				
		*ART***	*RRT****	*RRT*****	*RRT*\$*	*ART***	*RRT****	*RRT*****	*RRT*\$*	*RRT*\$\$*
1	2-Propen-1-ol	2.95	0.14	1.00	–	5.13	0.47	1.00	–	1.74
2	2-Propyn-1-ol	3.04	0.14	1.00	–	9.61	0.87	1.00	–	3.16
3	3-Buten-1-ol	3.61	0.17	1.00	–	6.10	0.55	1.00	–	1.69
4	4-Penten-2-ol	4.03	0.19	1.00	–	5.57	0.51	1.00	–	1.38
5	4-Penten-1-ol	5.20	0.24	1.00	–	8.68	0.79	1.00	–	1.67
6	*trans*-3-Hexen-1-ol	7.26	0.33	1.00	–	10.03	0.91	1.00	–	1.38
7	*cis*-3-Hexen-1-ol	7.37	0.34	1.00	–	10.48	0.95	1.00	–	1.42
8	2-Propenyl propanoate	5.95	0.27	2.02	1.00	5.06	0.46	0.99	1.00	0.85
9	2-Propynyl propanoate	6.22	0.29	2.05	1.00	8.74	0.79	0.91	1.00	1.41
10	3-Butenyl propanoate	8.12	0.37	2.25	1.00	6.39	0.58	1.05	1.00	0.79
11	1-Methyl-3-butenyl propanoate	9.11	0.42	2.26	1.00	6.28	0.57	1.13	1.00	0.69
12	4-Pentenyl propanoate	10.98	0.51	2.11	1.00	8.49	0.77	0.98	1.00	0.77
13	*trans*-3-Hexenyl propanoate	13.82	0.64	1.90	1.00	10.43	0.95	1.04	1.00	0.75
14	*cis*-3-Hexenyl propanoate	13.90	0.64	1.89	1.00	10.60	0.96	1.01	1.00	0.76
15	2-Propenyl 2-chloropropanoate	9.40	0.43	3.19	1.58	10.45	0.95	2.04	2.07	1.11
16	2-Propynyl 2-chloropropanoate	9.78	0.45	3.22	1.57	14.94	1.36	1.55	1.71	1.53
17	3-Butenyl 2-chloropropanoate	12.00	0.55	3.32	1.48	12.12	1.10	1.99	1.90	1.01
18	1-Methyl-3-butenyl 2-chloropropanoate	12.96	0.60	3.22	1.42	11.66	1.06	2.09	1.86	0.90
19	4-Pentenyl 2-chloropropanoate	14.79	0.68	2.84	1.35	14.31	1.30	1.65	1.69	0.97
20	*trans*-3-Hexenyl 2-chloropropanoate	17.42	0.80	2.40	1.26	15.99	1.45	1.59	1.53	0.92
21	*cis*-3-Hexenyl 2-chloropropanoate	17.52	0.81	2.38	1.26	16.22	1.47	1.55	1.53	0.93
22	2-Propenyl 3-chloropropanoate	11.20	0.52	3.80	1.88	13.73	1.25	2.68	2.71	1.23
23	2-Propynyl 3-chloropropanoate	11.56	0.53	3.80	1.86	17.75	1.61	1.85	2.03	1.54
24	3-Butenyl 3-chloropropanoate	13.82	0.64	3.83	1.70	15.31	1.39	2.51	2.40	1.11
25	1-Methyl-3-butenyl 3-chloropropanoate	14.83	0.68	3.68	1.63	14.99	1.36	2.69	2.39	1.01
26	4-Pentenyl 3-chloropropanoate	16.57	0.76	3.19	1.51	17.42	1.58	2.01	2.05	1.05
27	*trans*-3-Hexenyl 3-chloropropanoate	19.04	0.88	2.62	1.38	18.84	1.71	1.88	1.81	0.99
28	*cis*-3-Hexenyl 3-chloropropanoate	19.17	0.88	2.60	1.38	19.10	1.73	1.82	1.80	1.00

29	2-Propenyl butanoate	8.00	0.37	2.71	1.00	6.32	0.57	1.23	1.00	0.79
30	2-Propynyl butanoate	8.31	0.38	2.73	1.00	10.34	0.94	1.08	1.00	1.24
31	3-Butenyl butanoate	10.49	0.48	2.91	1.00	7.90	0.72	1.30	1.00	0.75
32	1-Methyl-3-butenyl butanoate	11.50	0.53	2.85	1.00	7.79	0.71	1.40	1.00	0.68
33	4-Pentenyl butanoate	13.36	0.62	2.57	1.00	10.17	0.92	1.17	1.00	0.76
34	*trans*-3-Hexenyl butanoate	16.01	0.74	2.21	1.00	12.08	1.10	1.20	1.00	0.75
35	*cis*-3-Hexenyl butanoate	16.06	0.74	2.18	1.00	12.26	1.11	1.17	1.00	0.76
36	2-Propenyl 2-chlorobutanoate	11.90	0.55	4.03	1.49	11.90	1.08	2.32	1.88	1.00
37	2-Propynyl 2-chlorobutanoate	12.22	0.56	4.02	1.47	16.21	1.47	1.69	1.57	1.33
38	3-Butenyl 2-chlorobutanoate	14.43	0.67	4.00	1.38	13.69	1.24	2.24	1.73	0.95
39	1-Methyl-3-butenyl 2-chlorobutanoate	15.30	0.71	3.80	1.33	13.24	1.20	2.38	1.70	0.87
40	4-Pentenyl 2-chlorobutanoate	17.02	0.78	3.27	1.27	15.69	1.43	1.81	1.54	0.92
41	*trans*-3-Hexenyl 2-chlorobutanoate	19.59	0.90	2.70	1.22	17.36	1.58	1.73	1.44	0.89
42	*cis*-3-Hexenyl 2-chlorobutanoate	19.68	0.91	2.67	1.23	17.58	1.60	1.68	1.43	0.89
43	2-Propenyl 3-chlorobutanoate	12.22	0.56	4.14	1.53	13.11	1.19	2.56	2.07	1.07
44	2-Propynyl 3-chlorobutanoate	12.57	0.58	4.13	1.51	17.20	1.56	1.79	1.66	1.37
45	3-Butenyl 3-chlorobutanoate	14.80	0.68	4.10	1.41	14.82	1.35	2.43	1.88	1.00
46	1-Methyl-3-butenyl 3-chlorobutanoate	15.71	0.72	3.90	1.37	14.55	1.32	2.61	1.87	0.93
47	4-Pentenyl 3-chlorobutanoate	17.42	0.80	3.35	1.30	16.96	1.54	1.95	1.67	0.97
48	*trans*-3-Hexenyl 3-chlorobutanoate	19.90	0.92	2.74	1.24	18.46	1.68	1.84	1.53	0.93
49	*cis*-3-Hexenyl 3-chlorobutanoate	19.99	0.92	2.71	1.24	18.68	1.70	1.78	1.52	0.93
50	2-Propenyl 4-chlorobutanoate	14.15	0.65	4.80	1.77	15.69	1.43	3.06	2.48	1.11
51	2-Propynyl 4-chlorobutanoate	14.50	0.67	4.77	1.74	19.61	1.78	2.04	1.90	1.35
52	3-Butenyl 4-chlorobutanoate	16.57	0.76	4.59	1.58	17.29	1.57	2.83	2.19	1.04
53	1-Methyl-3-butenyl 4-chlorobutanoate	17.42	0.80	4.32	1.51	16.89	1.53	3.03	2.17	0.97
	4-Pentenyl 4-chlorobutanoate	19.18	0.88	3.69	1.44	19.38	1.76	2.23	1.91	1.01
55	*trans*-3-Hexenyl 4-chlorobutanoate	21.52	0.99	2.96	1.34	20.85	1.89	2.08	1.73	0.97
56	*cis*-3-Hexenyl 4-chlorobutanoate	21.66	1.00	2.94	1.35	21.11	1.92	2.01	1.72	0.97
57	*n*-Tetradecane	21.69	1.00	–	–	11.01	1.00	–	–	0.51

* Absolute retention times (min) were measured from sample injection (Figs. 2–5).
** Relative retention time for *n*-tetradecane taken as 1.00.
*** Relative retention time for the corresponding alcohol taken as 1.00
§ Relative retention time for the corresponding unchlorinated ester taken as 1.00.
§§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.

propanoate (15) and *cis*-3-hexen-1-ol (7) are coincident and the peaks of the compound pairs 8 and 1, 5 and 9, 13 and 7, and 16 and 25 are only partially separated.

The poorer separations of a mixture of the alcohols (1–7) and their C_4-derivatives (29–56) could be achieved, as is shown in Figs. 4 and 5. 2-Propenyl 3-chlorobutanoate (43) and the 2-propynyl 2-chloro isomer (37) and also 4-pentenyl 3-chlorobutanoate (47) and 1-methyl-3-butenyl 4-chlorobutanoate (53) completely overlap on SE-30. In addition, *cis*-3-hexenyl 4-chlorobutanoate (56) and *n*-tetradecane (57) are coincident. As shown, a somewhat poorer resolution occurred between the *trans*- and *cis*-3-hexenyl esters (34 and 35, 41 and 42, 48 and 49, and 55 and 56) than for the corresponding C_3-derivatives. On OV-351, however, only 2-propenyl 4-chlorobutanoate (50) and 4-pentenyl 2-chlorobutanoate (40) are coincident, the peaks of the compound pairs 53 and 47, 44 and 52, and 52 and 41 partially overlapping.

Previously, Ashes and Haken[5] studied the retention behaviour of, *e.g.*, *trans*- and *cis*-3-hexenyl esters of lower (C_1–C_6) *n*-acids on packed aluminium columns coated with several non-polar and polar stationary phases under isothermal operating conditions. Generally, the esters are eluted in the same order as the alcohols, the *trans*-isomer being eluted first. However, according to their results, *cis*-3-hexenyl butanoate (35) is eluted earlier than the *trans*-isomer (34) on the following stationary phases: polydiphenylsiloxane (100% Phenyl), DC-230, DC-530, F-400 and F-500, *i.e.*, on both donor and acceptor stationary phases. The corresponding reversed elution

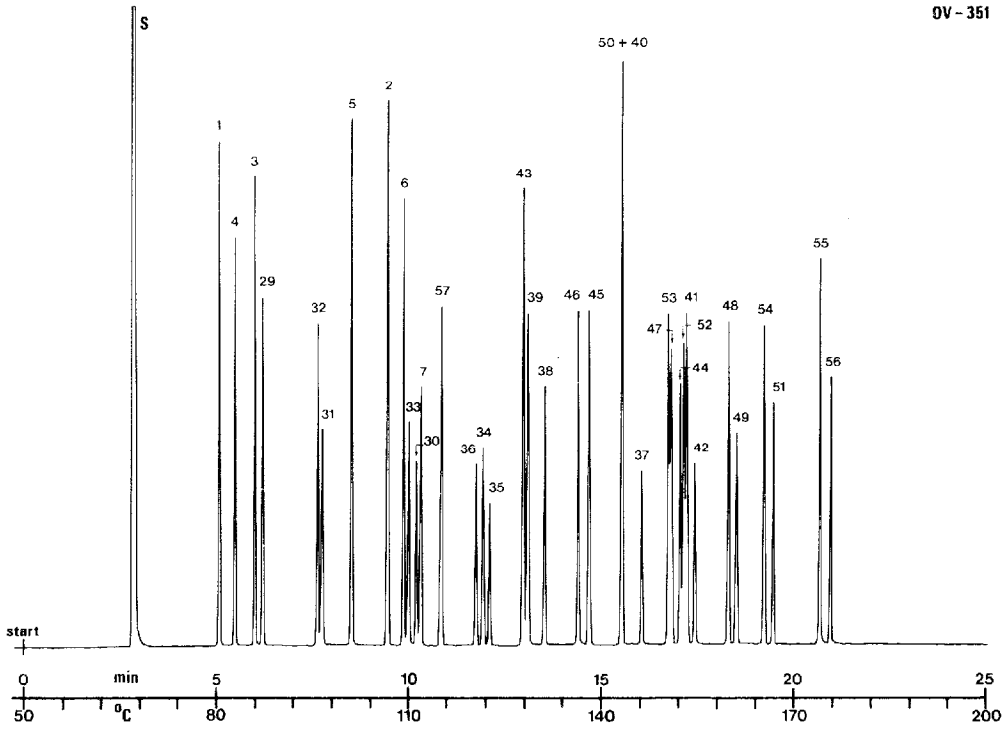

Fig. 5. Chromatogram of a mixture of unsaturated alcohols (1–7) and their butanoyl (29–35), 2-chlorobutanoyl (36–42), 3-chlorobutanoyl (43–49) and 4-chlorobutanoyl derivatives (50–56), analysed on OV-351. S = Solvent, *n*-tetradecane (57); compounds are identified in Table I.

orders did not occur within the other esters studied[5]. The present GC analyses of 3-hexen-1-ols and their derivatives were performed using a mixture of the *trans*- and *cis*-isomers. The observed ratio (60:40) of the peak areas showed that the alcohols (6 and 7) and all their derivatives (13 and 14, 20 and 21, 27 and 28, 34 and 35, 41 and 42, 48 and 49, and 55 and 56) are eluted in the same order on both SE-30 and OV-351 capillary columns. The identification of the isomers was based on the retention order of the *trans*- and *cis*-3-hexenyl propanoates and butanoates on the non-polar SE-30 and on the most polar XF-1150 stationary phases[5], the *trans*-isomer being assumed to elute first also on the capillary columns used.

Table I shows that the relative retention times, relative to *n*-tetradecane (57), varied on SE-30 between 0.14 and 1.00 and on OV-351 between 0.46 and 1.92. The retention (relative to the corresponding alcohol) is maximized on SE-30 for 1-methyl-3-butenyl propanoate (11), the 3-butenyl esters (17, 24 and 31) and the 2-propenyl monochlorobutanoates (36, 43 and 50) and minimized for all the *cis*-3-hexenyl esters (14, 21, 28, 35, 42, 49 and 56). On OV-351, the retention is maximized for the 1-methyl-3-butenyl esters (11, 18, 25, 32, 39 and 46) and 2-propenyl 4-chlorobutanoate (50) and minimized for the 2-propynyl esters (9 and 30) and the *cis*-3-hexenyl esters (21, 28, 42, 49 and 56). The last column in Table I shows that 2-propyn-1-ol (2) and its derivatives (9, 16, 23, 37, 44 and 51) and 1-methyl-3-butenyl butanoate (32) show the greatest disparities in retention behaviour on the columns used.

The comparison of the retention behaviour of the unsaturated esters studied in the present paper and of the corresponding saturated esters reported previously[1–3] shows that the retention order generally follows that of the alcohols presented in Fig. 1. Only 2- and 3-chloropropyl propanoates[1] and the corresponding 2-propynyl esters (16 and 23) are eluted on SE-30 in reversed order. In addition on OV-351 all the 2-propynyl esters (9, 16, 23, 30, 37, 44 and 51) were eluted earlier than the corresponding hexyl esters[1–3].

ACKNOWLEDGEMENTS

Financial support for this work was provided by the Foundation for Research on Natural Resources in Finland and the Leo and Regina Wainstein Foundation. This aid is gratefully acknowledged.

REFERENCES

1 I. O. O. Korhonen, *J. Chromatogr.*, 268 (1983) 229, and references cited therein.
2 I. O. O. Korhonen, *J. Chromatogr.*, 268 (1983) 437, and references cited therein.
3 I. O. O. Korhonen, *J. Chromatogr.*, 270 (1983) 171, and references cited therein.
4 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 101 (1974) 103, and references cited therein.
5 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 111 (1975) 171, and references cited therein.